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(54) INK JET RECORDING MEDIUM

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an ink jet recording medium having superior resistance to color change, ink absorbability, resistance to feathering and resistance to humidity.

SOLUTION: In the ink jet recording medium, a resin composition containing (A) a polyvinyl alcohol resin containing an acetoacetic ester and (B) a reducer is added in a base and/or in a coated layer on the surface of the base.

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CLAIMS

[Claim(s)]

[Claim 1] (A) The record medium for ink jets with which the resin constituent containing acetoacetic ester radical content polyvinyl alcohol system resin and the (B) reducing agent is characterized by coming to contain in a base material and/or the coating layer on the front face of a base material.

[Claim 2] (B) The record medium for ink jets according to claim 1 with which the content of a reducing agent is characterized by 0.01 – five-mol being % to one mol of acetoacetic ester radicals in (A) acetoacetic ester radical content polyvinyl alcohol system resin.

[Claim 3] (A) The record medium for ink jets according to claim 1 or 2 with which the acetoacetic ester radical content in acetoacetic ester radical content polyvinyl alcohol system resin is 0.1-10-mol %, and whenever [saponification / of this polyvinyl alcohol system resin] is characterized by 80-99.9-mol being %.

[Claim 4] (B) claims 1-3 characterized by a reducing agent being at least one sort chosen from a hydrogensulfite, dithionite, phosphite (degree), a hydrazine compound, sulfides, amino acid, and a citric acid -- either -- the record medium for ink jets of a publication.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the record medium for ink jets excellent in color fastness, the absorptivity of ink, feather-proof ring nature, moisture resistance, etc. in more detail about the record medium for ink jets.

[0002]

[Description of the Prior Art] It makes the ink made into the shape of a globule fly on the front face of recorded media, such as paper and PET, the ink jet recording method is the approach of recording an alphabetic character etc., and since there is an advantage, like there are few sounds at the time of printing which can perform multicolor printing which can perform high-speed printing, recently, it has come to be used abundantly.

[0003] And using acetoacetic ester radical content polyvinyl alcohol system resin for an ink acceptance layer, a topcoat layer, etc. for the purpose of improvement in the water resisting property of the printing section or weatherability is indicated by JP,61-125878,A, JP,10-181189,A, JP,10-193778,A, etc.

[0004]

[Problem(s) to be Solved by the Invention] However, if acetoacetic ester radical content polyvinyl alcohol system resin is used, although a water resisting property will improve, the trouble said that color fastness falls may occur and an improvement of color fastness is just going to desire.

[0005] That is, the place made into the purpose of this invention is offering the record medium for ink jets which was excellent in color fastness and was further excellent also in the absorptivity of ink, feather-proof ring nature, and moisture resistance.

[0006]

[Means for Solving the Problem] Then, the record medium for ink jets which the resin constituent containing (A) acetoacetic ester radical content polyvinyl alcohol system resin and the (B) reducing agent comes to contain in a base material and/or the coating layer on the front face of a base material finds out solving the above-mentioned technical problem, and this invention person etc. came to complete this invention, as a result of repeating research wholeheartedly in view of this situation.

[0007]

[Embodiment of the Invention] This invention is explained in detail below.

[0008] (A) acetoacetic ester radical content polyvinyl alcohol system resin (it may be hereafter written as the AA-ization PVA) used for this invention It is the thing which diketene was made to react to PVA, or made PVA and acetoacetic ester react and the ester interchange was carried out [thing] so that it might mention later, and made the acetoacetic ester radical introduce into PVA. As this PVA, the saponification object which generally saponified the lower alcohol solution of polyvinyl acetate according to saponification catalysts, such as alkali and an acid, or its derivative is used. The saponification object of the copolymer of vinyl acetate, the monomer which has copolymeric, and vinyl acetate etc. can also be used. Furthermore, as this monomer For example, ethylene, a propylene, an isobutylene, alpha-octene, alpha-dodecen, Olefins, such as alpha-octadecene, an acrylic acid, a methacrylic acid, a crotonic acid, partial saturation, such as a maleic acid, a maleic anhydride, and an itaconic acid, -- acids, its salt, monochrome, or dialkyl ester Nitril, such as acrylonitrile and meta-

acrylonitrile, acrylamide, Amides, such as methacrylamide, an ethylene sulfonic acid, an allyl compound sulfonic acid, Olefin sulfonic acids, such as a meta-allyl compound sulfonic acid, or the salt of those, and alkyl vinyl ether N-acrylamide methyl trimethylammonium chloride, allyl compound trimethylammonium chloride, Dimethyl diaryl ammonium chloride, a dimethyl allyl compound vinyl ketone, N-vinyl pyrrolidone, a vinyl chloride, a vinylidene chloride, the polyoxyethylene (meta) allyl compound ether, The polyoxyalkylene (meta) allyl compound ether, such as the polyoxypropylene (meta) allyl compound ether, Polyoxyalkylene (meta) acrylate, such as polyoxyethylene (meta) acrylate and polyoxypropylene (meta) acrylate, Polyoxyalkylene (meta) acrylamides, such as polyoxyethylene (meta) acrylamide and polyoxypropylene (meta) acrylamide, Polyoxyethylene (1-(meta) acrylamide -1, 1-dimethyl propyl) ester, Polyoxyethylene vinyl ether, polyoxypropylene vinyl ether, polyoxyethylene allylamine, polyoxypropylene allylamine, a polyoxyethylene vinyl amine, a polyoxypropylene vinyl amine, etc. are mentioned. PVA used as the raw material of this formation PVA of (A) AA Although not limited especially, whenever [saponification / 80-99.9 mol% (further 88-97 mol %, especially 92-96-mol %) of] is desirable. Whenever [this saponification] less than [80 mol %] When a water resisting property falls, 99.9-mol % was exceeded conversely and it uses for the coating application of the record medium for ink jets, it becomes and is not desirable, if the ink acceptance nature of water color ink falls when it uses especially for an ink acceptance layer.

[0009] Moreover, 500-5000 (further 1200-5000, especially 1700-3000) are desirable, and if adhesion with an ink acceptance layer falls and the average degree of polymerization of PVA exceeds 5000 conversely when this average degree of polymerization uses for the coating application of the record medium for ink jets less than by 500, it worsens and is not desirable [average degree of polymerization / the coating nature at the time of this coating].

[0010] (A) Although the approach to which PVA and diketene like the above are made to react, the approach of making PVA and acetoacetic ester react and carrying out an ester interchange, the approach of carrying out copolymerization of vinyl acetate and the acetoacetic-acid vinyl, etc. can be mentioned in order to obtain the AA-ization PVA, a production process is simple and it is desirable to manufacture from the point that the quality AA-ization PVA is obtained, by the approach to which PVA (powder) and diketene are made to react. After carrying out the direct reaction of the diketene PVA, a gas, or liquefied as an approach to which PVA and diketene are made to react and carrying out adsorption occlusion of the organic acid to PVA beforehand, the approach of spraying the diketene of liquefied or a gas, reacting under an inert gas ambient atmosphere, or spraying the mixture of an organic acid and liquefied diketene on PVA, and reacting to it is used.

[0011] It is enough if it is equipment to which it could warm and the agitator was attached as a reactor at the time of carrying out the above-mentioned reaction. For example, a kneader, a Henschel mixer, a ribbon blender, other various blenders, and a churning dryer can be used. As for the content of the acetoacetic ester radical of the formation PVA of (A) AA obtained in this way, it is desirable to consider as 0.1 - ten-mol % (further 2-8-mol %, especially 3-5-mol %), and if the water resisting property in an ink acceptance layer or a topcoat layer may fall less than [0.1 mol %] and this content exceeds ten-mol % conversely, it is not missing [of coating liquid / with time], and desirable.

[0012] Moreover, as for the starting formation PVA of (A) AA, it is desirable that the content of sodium acetate is 0.1 or less (further 0.01 - 0.05 % of the weight, especially 0.01 - 0.03 % of the weight) % of the weight, and if this content exceeds 0.1 % of the weight, it falls and is not desirable [the formation / the water resisting property in an ink acceptance layer or a topcoat layer]. This content can be adjusted by the approach of a methanol etc. washing the (A) AA-ization PVA.

[0013] If a reduction operation is done to the above-mentioned AA-izing PVA, the (B) reducing agent used for this invention it limits especially -- not having -- for example, a sulfite (a sodium sulfite and potassium sulfite --) thiosulfates (a sodium thiosulfate and potassium thiosulfate --), such as ammonium sulfite hydrogensulfites (a sodium hydrogensulfite --), such as ammonium thiosulfate metabolisulfite (the sodium metabolisulfite --), such as hydrogen sulfite ammonium dithionite (a sodium dithionite --), such as potassium metabolisulfite phosphite (degree) (sodium hypophosphite --), such as a dithionic acid potassium Hypophosphorous acid ammonium, calcium hypophosphite, a hypophosphorous acid potassium, etc., L-ascorbic acid and a hydrazine compound (hydrazine sulfate and hydrazine hydrochloride --) A carbonic acid hydrazine, a permutation hydrazine, a phosphoric-acid

hydrazine, methylhydrazine, etc., Sulfides (a dibenzyl sulfide, hexyl methyl sulfide, etc.) Amino acid, organic acids (an aspartic acid, glutamic acid, glycine, etc.) (a citric acid, formic acid, oxalic acid, malonic acid), the salts (malonic-acid sodium etc.) of those, etc. can be mentioned. Suitably At least one sort chosen from a hydrogensulfite, dithionite, phosphite (degree), a hydrazine compound, sulfides, amino acid, and an organic acid is used, and a sodium hydrogensulfite and a sodium dithionite are used especially preferably.

[0014] Although especially the amount about (A) and (B) contained in a resin constituent is not limited, the content of (B) to (A) (A -- one mol of inner acetoacetic ester radicals -- receiving -- 0.01 - five-mol % (further 0.01-2-mol % --) It is especially [0.01-1 mol% of] desirable, and if the addition effectiveness of a reducing agent does not have this content less than [0.1 mol %], the printing section passes and five-mol % is exceeded for discoloration by the time to a lifting or the reverse which becomes empty, neither a water resisting property nor weatherability falls and is desirable. Although the resin constituent containing the formation PVA of (A) AA and the (B) reducing agent like the above is used in this invention It is desirable to also make a deck-watertight-luminaire-ized agent contain for the purpose of the waterproof improvement in a topcoat layer. Furthermore, as this deck-watertight-luminaire-ized agent Glyoxal, a urea-resin, polyamine polyamide epichlorohydrin, polyethyleneimine, 3, the cation-ized resin of a quaternary-ammonium-salt mold, a glyoxylic acid, amide resin, GURISHIJIN, isocyanate, etc. can be mentioned, and glyoxal is used suitably. If 0.01 - five-mol % (further 0.01-2.5-mol %, especially 0.01-1.5-mol %) is desirable, and this content exceeds five-mol % conversely as a content of this deck-watertight-luminaire-ized agent to one mol of acetoacetic ester radicals under formation PVA of (A) AA rather than has enough deck-watertight-luminaire-ized effectiveness less than [0.01 mol %], the stability of coating liquid falls and is not desirable.

[0015] Moreover, also in sinking [which is mentioned later] in (content) and/or the base material by which coating is carried out, in raising a whiteness degree etc., it is desirable that the non-subtlety particle is blended, as this non-subtlety particle, a synthetic silica, colloidal silica, an alumina, etc. can be mentioned and silicon compounds, such as a synthetic silica and colloidal silica, are suitably used into this resin constituent. As a configuration of this non-subtlety particle, the shape of the shape of a globular shape, a grain, and powder and a rosary etc. is mentioned. Moreover, as the mean particle diameter 0.01-50 micrometers (further 0.05-30 micrometers, especially 0.1-20 micrometers) are desirable. It is in the condition that were hard to apply this particle diameter in less than 0.01 micrometers since the fluidity of coating liquid was bad, and the diameter of an ink dot was small, print concentration became low, smooth nature fell when 50 micrometers was exceeded conversely, and the front face was rough and is not desirable.

[0016] The loadings of this non-subtlety particle are the 0.1 - 100 weight section (0.1 - 50 weight section, especially 0.1 - 10 weight section are still more desirable, and in under the 0.1 weight section, if it becomes easy to produce a blot of an alphabetic character and these loadings exceed the 100 weight sections conversely, they become easy to produce the fall of coloring concentration and are not desirable.) to this resin constituent 100 weight section. When the amount of a non-subtlety particle is lessened when transparency is required like the film for OHP (overhead project) with a natural thing (the amount of concrete is 0.1 - 10 weight section extent), and white is required like paper, what the amount of a non-subtlety particle is made [many] for (the amount of concrete is 10 - 50 weight section extent) is desired.

[0017] Moreover, to the resin constituent used by this invention, if needed, if it is the range which can also add well-known additives, such as a defoaming agent, a release agent, surface active agents (a silicon system, a fluorine system, polyethylene-glycol system, etc.), antiseptics, an insecticide, a rust-proofer, and a thickener, and does not spoil the description of this invention, resin, such as other paper processing agents, for example, other well-known polyvinyl alcohol, starch, a carboxymethyl cellulose, an acrylic latex, and an SBR latex, is also conventionally mixable. In this invention, although the resin constituent like the above contains in the coating layer on the inside of a base material, and/or the front face of a base material, although there is especially no limit, as this base material, paper of fine quality, a report grade paper, glassine (semi), glossy paper, coat paper, a PET sheet, a PVC sheet, a PEN (polyethylenenaphthalate) sheet, a PET film, a PVC film, a PEN film, etc. are used

suitably, for example.

[0018] In carrying out coating of the resin constituent to this base material, the approach of well-known arbitration, such as a size press coat, the roll coater method, an EYA Doctor process, the blade coating-machine method, and the gate roll coater method, is adopted, but when carrying out coating of this resin constituent, it is desirable that solid content considers as 1 - 70% of the weight (further 2 - 60 % of the weight, especially 5 - 50 % of the weight) of a water solution. This solid content at less than 1 % of the weight There is little coating weight, and since print concentration and surface paper durability reinforcement also become a low thing lacking in practicality, coating becomes difficult since the viscosity of coating liquid will become high if 70 % of the weight is exceeded conversely, and coating spots are also produced, it is not desirable. It is appropriate for the coverage of the resin constituent by which coating is carried out to a base material to make it 0.1 - 40 g/m² (solid content conversion) and the (A) AA-ization PVA become 0.5 - 20 g/m² (same as the above) extent preferably especially.

[0019] In this way, this resin constituent contains in the coating layer on the inside of a base material, and/or the front face of a base material, and the record medium for ink jets of this invention is obtained.

[0020]

[Example] Hereafter, an example is given and this invention is explained concretely.

[0021] In addition, among an example, especially, that it is with the "section" and "%" shows weight criteria, as long as there is no notice.

[0022] The example 1AA-ized PVA[average degree of polymerization 1700 and whenever [saponification] 94-mol %, After dissolving the 0.03%]5 of acetoacetic ester radical content % and sodium acetate contents of 4.0 mols section in the water 234.75 section, an amorphous synthetic silica (the Fuji SHIRISHIA chemistry company make and "SAISHIRIA 446" --) Configuration : 0.25 section (it is 1.08-mol % to one mol of acetoacetic ester radicals under AA-izing PVA) addition of a globular form, the particle diameter:4.5-micrometer ten sections, and the glyoxal is carried out by solid content conversion. The water solution was obtained, to the water-solution 100 obtained section, 0.4% of sodium-hydrogensulfite water-solution 1 section (it is 0.024-mol % to one mol of acetoacetic ester radicals under AA-izing PVA) was added as a reducing agent, and the water solution of a resin constituent was obtained.

[0023] Subsequently, the water solution of the obtained resin constituent was used as coating liquid, coating of this coating liquid was carried out to the paper of fine quality of basis-weight 100 g/m² by the 500-micrometer applicator, it was dried for 2 minutes at 105 degrees C with the cylinder rotating type dryer after that, and the record medium for ink jets of this invention was obtained.

[0024] The ink jet printer ("PM-770C" by Seiko Epson) performed solid printing to the obtained record medium for ink jets, and the following evaluations were performed to it. (Color fastness) The printed record medium was left for one month under the ambient atmosphere of 40 degrees C and 90%RH, visual observation was carried out and the discoloration degree at that time was evaluated as follows.

[0025]

O --- O as which discoloration is not regarded at all --- ** as which discoloration is hardly regarded --- x as which discoloration is regarded a little --- Discoloration after [of printing] 1 remarkable (absorptivity of ink) minute A PPC copy paper is put on the printing side of a record medium, and it is a hand roller (die length of 20cm of the roller section) from this copy paper. Visual observation of the imprint condition of the ink to this copy paper when grinding 5 times was carried out so that the load of 5kgf(s) (49Ns) might be applied using the diameter of 8cm and it might not go in the die-length direction, and it evaluated as follows.

[0026]

O --- ** as which the imprint of ink is not regarded --- x as which the imprint of ink is regarded a little --- The imprint of ink carried out visual observation and evaluated the blot (feather ring) situation of the printing part immediately after remarkable (feather-proof ring nature) printing as follows.

[0027]

O --- ** as which a blot is hardly regarded --- x as which a blot is regarded a little --- The blot left

the printed remarkable (moisture resistance) record medium for one month under the ambient atmosphere of 40 degrees C and 90%RH, and evaluated the breadth situation of a blot of the printing part at that time as compared with immediately after printing as follows.

[0028]

O --- ** in which a blot has hardly spread --- x in which the blot has spread a little --- Except the blot having used 2% of sodium-hydrogensulfite water solution as a reducing agent in example 2 example 1 which has spread remarkably the 1 section (it being 0.12-mol % to one mol of acetoacetic ester radicals under AA-izing PVA), it carried out similarly, the record medium for ink jets was obtained, and it evaluated similarly.

[0029] In example 3 example 1, except having used 4% of sodium-hydrogensulfite water solution as a reducing agent the 1 section (it being 0.24-mol % to one mol of acetoacetic ester radicals under AA-izing PVA), it carried out similarly, the record medium for ink jets was obtained, and it evaluated similarly.

[0030] In example 4 example 1, except having changed whenever [saponification / of the AA-izing PVA] to 96-mol%, it carried out similarly, the record medium for ink jets was obtained, and it evaluated similarly.

[0031] In example 5 example 1, except having changed the average degree of polymerization of the AA-izing PVA into 2600, it carried out similarly, the record medium for ink jets was obtained, and it evaluated similarly.

[0032] In example 6 example 1, except having used 0.7% of sodium-dithionite water solution as a reducing agent the 1 section (it being 0.025-mol % to one mol of acetoacetic ester radicals under AA-izing PVA), it carried out similarly, the record medium for ink jets was obtained, and it evaluated similarly.

[0033] In example 7 example 1, except having used 0.5% of sodium-phosphite water solution as a reducing agent the 1 section (it being 0.025-mol % to one mol of acetoacetic ester radicals under AA-izing PVA), it carried out similarly, the record medium for ink jets was obtained, and it evaluated similarly.

[0034] In example 8 example 1, except having used 0.15% of hydrazine water solution as a reducing agent the 1 section (it being 0.03-mol % to one mol of acetoacetic ester radicals under AA-izing PVA), it carried out similarly, the record medium for ink jets was obtained, and it evaluated similarly.

[0035] In example 9 example 1, except having used 0.85% of dibenzyl sulfide water solution as a reducing agent the 1 section (it being 0.025-mol % to one mol of acetoacetic ester radicals under AA-izing PVA), it carried out similarly, the record medium for ink jets was obtained, and it evaluated similarly.

[0036] In example 10 example 1, except having used 0.6% of glutamic-acid water solution as a reducing agent the 1 section (it being 0.026-mol % to one mol of acetoacetic ester radicals under AA-izing PVA), it carried out similarly, the record medium for ink jets was obtained, and it evaluated similarly.

[0037] In example 11 example 1, except having used 0.75% of citric-acid water solution as a reducing agent the 1 section (it being 0.024-mol % to one mol of acetoacetic ester radicals under AA-izing PVA), it carried out similarly, the record medium for ink jets was obtained, and it evaluated similarly.

[0038] The example 12AA-ized PVA[average degree of polymerization 1700 and whenever [saponification] 94-mol %, After dissolving the 0.03%]10 of acetoacetic ester radical content % and sodium acetate contents of 4.0 mols section in the water 84.5 section, an amorphous synthetic silica (the Fuji SHIRISHIA chemistry company make and "SAISHIRIA 446" ---) Configuration : 0.5 section (it is 1.075-mol % to one mol of acetoacetic ester radicals under AA-izing PVA) addition of a globular form, the particle diameter:4.5-micrometer five sections, and the glyoxal is carried out by solid content conversion. The water solution was obtained, to the water-solution 100 obtained section, 2% of sodium-hydrogensulfite water-solution 1 section (it is 0.024-mol % to one mol of acetoacetic ester radicals under AA-izing PVA) was added as a reducing agent, and the water solution of a resin constituent was obtained.

[0039] Subsequently, the water solution of the obtained resin constituent was used as coating liquid, coating of this coating liquid was carried out to 100micromPET film (95% of transparencies) in thickness by the 500-micrometer applicator, it was dried for 10 minutes at 105 degrees C with the

cylinder rotating type dryer after that, and the record medium for ink jets of this invention was obtained.

[0040] About the obtained record medium for ink jets, it evaluated like the example 1.

[0041] In example 13 example 12, except having used 10% of sodium-hydrogensulfite water solution as a reducing agent the 1 section (it being 0.12-mol % to one mol of acetoacetic ester radicals under AA-izing PVA), it carried out similarly, the record medium for ink jets was obtained, and it evaluated similarly.

[0042] In example 14 example 12, except having used 20% of sodium-hydrogensulfite water solution as a reducing agent the 1 section (it being 0.24-mol % to one mol of acetoacetic ester radicals under AA-izing PVA), it carried out similarly, the record medium for ink jets was obtained, and it evaluated similarly.

[0043] In example of comparison 1 example 1, except having not blended a reducing agent, it carried out similarly, the record medium for ink jets was obtained, and it evaluated similarly.

[0044] The evaluation result of an example and the example of a comparison is shown in Table 1.

[0045]

[Table 1]

Color fastness	Absorptivity of ink	Feather-proof ring nature	Moisture resistance	Example 1	O O O O
** 2	O O O O	** 3	O O O O	** 4	O O O O
** 9	O O O O	** 10	O O O O	** 11	O O O O
					** 12 O O O O
					** 13 O O O O
					** 14 O O O O

Example 1 of O comparison x ** *** ** [0046]

[Effect of the Invention] Since the resin constituent which blended the reducing agent with the AA-ization PVA contains the record medium for ink jets of this invention in the coating layer on the inside of a base material, and/or the front face of a base material, although the color fastness made into a technical problem so far is improvable, the absorptivity of ink, feather-proof ring nature, and moisture resistance are also boiled, and are further excellent and it is very useful to the record medium for ink jets. It is also possible to use for a record device like the pen plotter which used water color ink besides the ink jet type, a writing instrument, etc.

[Translation done.]